THE DEVELOPMENT OF A HIGH EFFICIENCY NON-POROUS HYDROGEN DEPOLARIZED ANODE FOR FUEL CELLS

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During investigations of many types of anodes we have found that all conventional porous anodes suffer from the disadvantage that physical control of the three phase interface is necessary in order to stabilize the system and maintain an acceptable level of polarization. There are presently three ways of achieving this control over the meniscus:

1. The interface can be maintained by controlling the porosity of the electrode in the manner developed by F. T. Bacon[1], and generally known as the biporous electrode structure. Essentially this consists of two porous structures, the one facing the electrolyte having a mean pore size smaller than that of the coarse pore structure facing the gas phase. Thus by careful control of the differential pressure applied across the electrode, a stable interface is maintained somewhere within the electrode. If a certain differential pressure is exceeded, bubbling will commence at the largest pore in the fine pore layer.

2. Many other investigators have used the homoporous electrode structures, such as those described by Justi[2], which are used in a bubbling condition. This again necessitates a certain differential pressure at which an acceptable rate of bubbling occurs through some of the larger pores while a stable interface is maintained in pores of smaller diameter.

3. The third commonly used technique is to waterproof the electrode structure. This consists of applying a waterproofing layer to the surface of the porous structure, which apparently prevents gross flooding of the larger pores. Whether or not the smaller pores of the structure are flooded is not obvious. Likewise, electrodes can be constructed by incorporating waterproofing agents such as Teflon or Kel-F into a finely dispersed metal powder which is then fabricated into a porous layer.

All these three types of electrode have certain disadvantages such as the difficulty of controlling bubbling on waterproofed or homoporous structures with the consequent loss of fuel and its attendant dangers, or in the case of biporous structures quality control during manufacture is essential to achieve reproducible porous structures.

The case of true, solid electrolytes is, of course, unique, and it is more difficult to define interphase structures in the case of such systems as Pt/ion exchange membranes and Pt/ZrO_2-CaO.

However, it was evident that if a solid diffusion anode could be made by simple procedures, it would possess some unique advantages. With this object in view, we chose to investigate the palladium alloy systems as a possible way of making solid non-porous diffusion anodes.

PHYSICAL AND ELECTROCHEMICAL MECHANISMS INVOLVED

The processes occurring in the solid non-porous diffusion type electrode are shown in Figure 1. The first stage involves chemisorption and dissociation of the hydrogen accompanied by the formation of metal hydrogen bonds at the surface. The hydrogen then diffuses as a proton interstitially through the bulk metal; the nature of the diffusion mechanism at grain boundaries is not defined. On reaching the electrolyte surface of the membrane the protons emerge into specific bound surface states from which they are removed by the potential difference across the double layer. Thus the total process involves three distinct activation energies: activation energy of dissociation, activation energy of the bulk diffusion process, and the activation energy for the transfer of protons at the electrolyte interface. There exists a concentration gradient of protons across the membrane which provides the driving force for the diffusion process. Part of the investigation has been to determine the role of these various processes and the rate-controlling mass-transfer mechanisms.

EXPERIMENTAL PROCEDURES

During the development of this electrode both electrochemical studies and gaseous diffusion studies were carried out simultaneously. The diffusion studies will, however, be reported separately, but it will be noted that they have confirmed the findings of the electrochemical studies.

The electrochemical studies were carried out under controlled conditions of temperature and pressure using in most cases half cells, that is, the cathode of the cell consisted of a platinum gauze from which hydrogen was evolved. Certain of the early feasibility studies and the scale-up studies were conducted on cells containing oxygen depolarized cathodes. During the feasibility stage some of the electrodes investigated consisted of tubular structures of the type used for gaseous diffusion and separation of hydrogen. It had been hoped that these could be incorporated into concentric type cells giving high power density per unit volume, but the many problems associated with fabricating, sealing, and gasketing biporous tubular cathodes resulted in the use of more suitable designs. It was also found extremely difficult to calculate current-density distributions in cells using circular cross-section electrodes, i.e., tubes, unless the surrounding cathode was exactly concentric.

Polarization measurements were made in all cases against a hydrogen electrode which consisted of a palladium-silver tube containing hydrogen under pressure which acted as a non-polarizable reference. Thus, all potentials quoted are measured against the reversible hydrogen electrode in the same electrolyte under the same conditions (sometimes referred to as the E* scale).

Electrode dimensions were in most cases one-inch diameter flat membranes; in scale-up studies three-inch, five-inch and six-inch square electrodes were used. Except where stated, 75% Pd-25% Ag was the alloy used.

Electrolytes used during the studies consisted of USP grades of potassium hydroxide, sulfuric acid, and phosphoric acid over the temperature range from room temperature to 250°C.

Luggin capillaries were used to measure the potential at the electrode surface. All of the data presented here (except Figure 6) are steady state polarization data and do not include any data derived from galvanostatic transients. Thus all electrode IR drops are included in the measurements: i.e., those caused by conductor resistances.

FEASIBILITY STUDIES

Initial feasibility studies were conducted on 25% silver 75% palladium alloy membranes at temperatures up to 250°C. These early results were somewhat variable, but very encouraging. Limiting currents up to several amps/cm^2 were observed and polarizations of the order of 150 mV were obtained over the current density range of 200 to 400 amps/ft^2. However, at lower temperatures occasional irreproducibility and varying rates of surface poisoning prompted a study of surface treatment and preparation.

THE EFFECTS OF SURFACE PRE-TREATMENT

The effects of surface preparation are shown in Figure 2, which clearly indicates the effect of treating of gas and electrolyte surfaces separately and in combination. In order to demonstrate the effects clearly, polarization values are shown for various membranes at 150°C. Pre-treatment of the electrolyte surface has a significant effect on the activation polarization and has obviously resulted in a much more active surface, either by lowering the activation energy of the process or by increasing the number of sites available. Limiting currents are not affected however. Activation of the gas surface demonstrates a marked effect on the limiting current density obtainable from the membranes, confirming as we had suspected that the surface absorption and dissociation processes were a rate controlling mechanism. It is of interest to note also that pre-treatment of the gas-side surface has an effect on the "activation-polarization" region as well as limiting currents. This is in fact accounted for by the increased diffusion of hydrogen to the electrolyte surface resulting in a greater concentration of hydrogen in the double layer. This increases the pre-exponential factor in the rate equation, resulting in higher currents at a given polarization value. The combination of gas and electrolyte side pre-treatment results in an electrode having both high limiting currents and low polarization.

Diffusion studies conducted concurrently confirmed the results of the electrochemical investigation, namely, that at lower temperatures the surface processes were rate controlling. However limiting currents are always somewhat larger than those predicted from diffusion experiments. The probable explanation of this anomaly is that on polarizing the electrode a very low pressure of hydrogen

exists at the electrolyte interface. Taking a very simple view, the electrochemical process eliminates the recombination step: $H + H \rightarrow H_2$. The removal of H from the surface under conditions of polarization can be far more rapid than desorption of H_2.

The investigation of surface treatment indicates clearly that the "electrolyte-surface" is potential-controlling while the "gas-surface" is rate-controlling.

From a practical point of view, this phase of the investigation resulted in methods of preparing the diffusion electrodes with extremely good reproducibility and with a minimum need for quality control procedures.

Having easily reproducible electrodes available, a series of parametric investigations were conducted.

TEMPERATURE DEPENDENCE

The effects of temperature on polarization and limiting currents are shown in Figure 3 over the range from room temperature to 200°C. Although at room temperature polarization is considerably increased, limiting currents of the order of 300 to 400 mA/cm^2 are still obtainable and the electrode can provide adequate starting power from ambient. Above 100°C the measurement of limiting current becomes extremely difficult due to the very high current values involved. For example, measurements at 200°C have indicated limiting currents in the region of 3,500 to 4,000 $amps/ft^2$; it is virtually impossible to measure such high limiting currents with accuracy.

DURABILITY OF THE ANODES

Many anodes of various sizes have been investigated for periods up to 500 hours under varying load conditions. Corrosion appears to be the only factor controlling electrode durability. However, since the corrosion potential of palladium silver is some 800 mV positive to hydrogen, only complete poisoning of the electrode surface can result in such excessive polarization and subsequent corrosion. It has been our experience using the electrolytes described and gases of commercial purity that this situation does not, in fact, arise and there appears to be no theoretical limit to the lifetime of the electrodes.

THE EFFECT OF ELECTROLYTE COMPOSITION

The effect of electrolyte concentration has been studied and there appears to be no particular effect on polarization or limiting current over the composition ranges of interest. Naturally the specific resistivity of the electrolyte varies and this can, of course, affect the over-all polarization of the cell. The lack of invariance with electrolyte concentration indicates the minimum importance of concentration polarization at the surface due to electrolyte species.

Polarization in acidic or basic electrolytes is similar.

THE LIMITING EFFECTS OF HYDROGEN PARTIAL PRESSURE

A study of the partial pressure effects of hydrogen indicated that partial pressure has little or no effect on polarization until limiting current density regions are approached. The effects of partial pressure of hydrogen on limiting current density is demonstrated in Figure 4. It will be noted that significant current densities can be sustained at partial pressures of hydrogen as low as 1 psia.

In connection with our original concept for a solid, diffusion-anode capable of operating with impure hydrogen streams, this is an extremely important finding since it determines the degree of utilization of the fuel. For example, if the limiting current density acceptable is 150 mA/cm^2, then the partial pressure of hydrogen in the purge gas, i. e. , the gas being discarded from behind the electrode, would be approximately 1 psia. If the in-going partial pressure of hydrogen is atmospheric, i. e. , 15 psia, this would represent about 93% utilization of the hydrogen. An in-going partial hydrogen pressure of 25 psia would result in 96% fuel utilization.

THE EFFECTS OF MEMBRANE THICKNESS

The effects of membrane thickness on the polarization and limiting current are shown in Figure 5. The effects on polarization at current densities below the limiting current density region are negligible. Limiting current density, however, is an inverse function of thickness for a given partial pressure of hydrogen, thus indicating that performance, as well as economics, can be improved by the use of extremely thin membranes.

STUDY OF POISONING EFFECTS

A comprehensive study of poisoning has been conducted. Poisoning of the electrode/electrolyte interface is of course effected (as are all metal surfaces) by excessive amounts of heavy metal ions and chloride ions but in all cases using USP grades of electrolyte and distilled water no deterioration in performance has been observed under working conditions.

A comprehensive study of poisoning of the gas surface has been made including in the hydrogen-containing streams hydrocarbons, methanol, formaldehyde, formic acid, CO, CO_2, ammonia, nitrogen, and water. By control of flow rates and conditions on the gas side of the membrane, none of the above-mentioned materials have been observed to cause significant polarization effects.

The studies of sulfur impurities and trace metals such as vanadium have not been completed. It is difficult at this time to predict in what form and in what quantity these particular elements might occur in reformed streams. Also if a reformer stream is used for the fuel cell we do not expect the membrane to be any more susceptible to poisoning than the reforming catalyst, which may, in fact, remove selectively some of the undesirable materials such as sulfur and vanadium. Generally speaking, we can expect sulfur poisoning to become more important at lower temperatures. Carbon deposition on the gas surface has never been observed.

An interesting effect, which is a form of poisoning has been studied. The effect was reported by Darling[3] in the course of hydrogen diffusion studies through palladium. He observed that even when using electrolytic hydrogen of high purity, that a constant diffusion rate could only be maintained by "purging" the high pressure side of the membrane. We observed the same phenomenon with "pure" hydrogen using the Pd-Ag anode. If the gas-vents were closed, a steady increase in polarization ensued. An experiment in which the "pure" (electrolytic) hydrogen was first diffused through Pd-Ag and then supplied to the Pd-Ag anode resulted in the disappearance of the phenomenon. It can only be concluded that an impurity is present in small quantities and since the "Darling effect" is observed over a range of temperature from ambient to 600°C, it is likely that the impurity does not chemisorb or physically adsorb. Most probably it accumulates in surface micro-pores restricting hydrogen diffusion to active sites on the metal surface of such pores and cracks.

ELECTROCHEMICAL CHARACTERISTICS OF THE SOLID DIFFUSION ELECTRODE

Polarization values for the electrode at 200°C derived by transient techniques are shown in Figure 6 plotted on a semi-log basis. It would appear, as might have been predicted, that the electrode exhibits Tafel behaviour. Unfortunately because of the large currents involved it has not been possible to study the electrode polarization far into the linear Tafel region; IR contributions become excessively large. Essentially, at practical current densities the electrode polarization is in the non-linear Tafel region.

THE EFFECT OF MEMBRANE COMPOSITION

The effects of various alloy compositions were studied and results are shown in Figure 7. The 25% silver 75% palladium alloy demonstrates superior polarization and higher limiting currents than all other compositions studied and there appears to be little economic advantage at this stage to increasing the amount of silver in the alloy.

SCALE-UP STUDIES

Scale-up studies have been conducted on electrodes from one inch diameter to six inch square size. Results are shown in Figure 8 for electrodes of one, and five inch diameter. The differences in polarization behaviour are not significant.

FUTURE APPLICATIONS OF THE ELECTRODES

This non-porous diffusion anode has been developed to the stage where reproducibility and simplicity of manufacture have been amply demonstrated. Its extreme thinness and ability to handle high current densities make it intrinsically suitable for very high power density systems.

Further, its ability to handle impure streams of hydrogen and its low susceptibility to poisoning show it to be an electrode which is extremely suitable for use with reformer streams using cheap hydrocarbons, methanol or ammonia, as fuel. Its ability to operate in alkaline or acid electrolyte make it a versatile anode, as does the fact that it can operate at negative, zero, or positive differential pressures.

The authors acknowledge the technical contributions and experimental studies of Mr. F. Malaspina and the results of the diffusion studies conducted by Mr. N. I. Palmer.

LITERATURE CITED

(1)   British Patent 667, 298
(2)   United States Patent 2, 860, 175
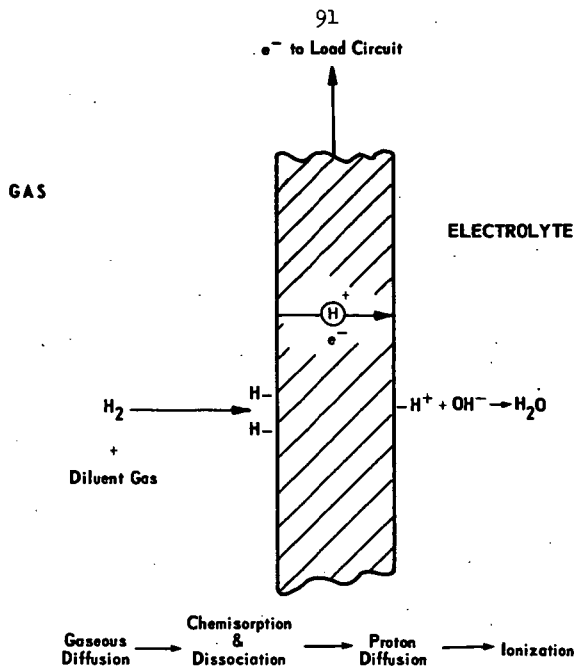(3)   Darling, A. S., Plat. Met. Rev., 2, 16, (1958)

e⁻ to Load Circuit

GAS

ELECTROLYTE

(H)⁺
e⁻

H₂ ——→ H—
—H⁺ + OH⁻ —→ H₂O
+ H—
Diluent Gas

Gaseous ——→ Chemisorption & ——→ Proton ——→ Ionization
Diffusion   Dissociation   Diffusion

Figure 1 — Sequence of Mechanisms Involved at Non-Porous Anode

Electrode: 75% Pd–25% Ag
Counter Electrode: Pt
Electrolyte: KOH

Anode Polarization

④

②

③

①

Type Of Preparation

① Electrolyte Side
② Gas Side
③ Both Sides
④ Unactivated
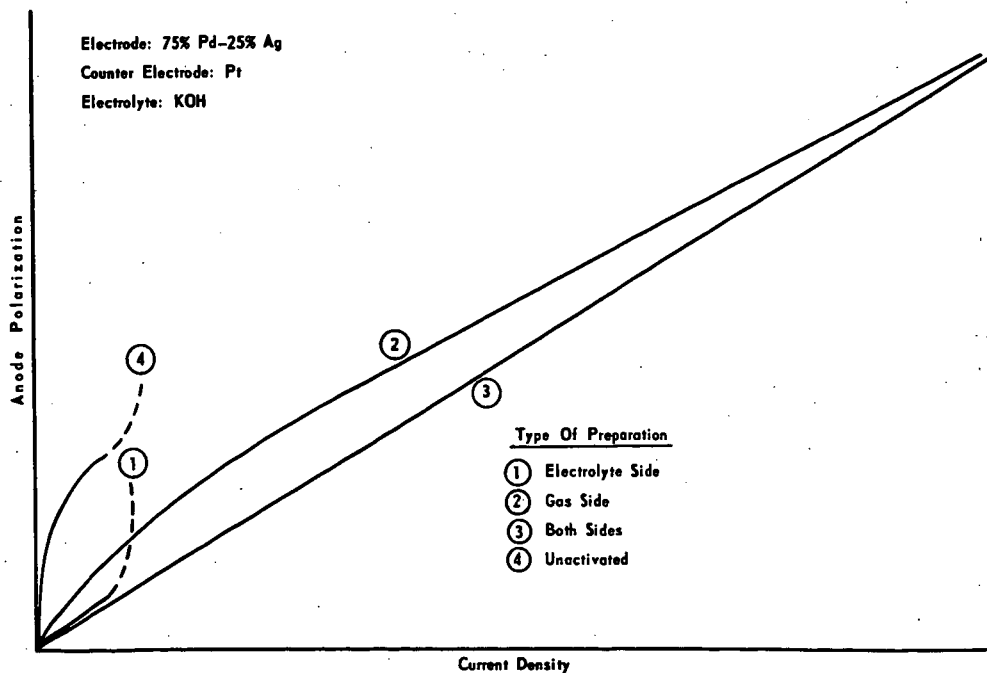
Current Density

Figure 2 — Effect of Surface Preparation on Polarization of Membrane Anode
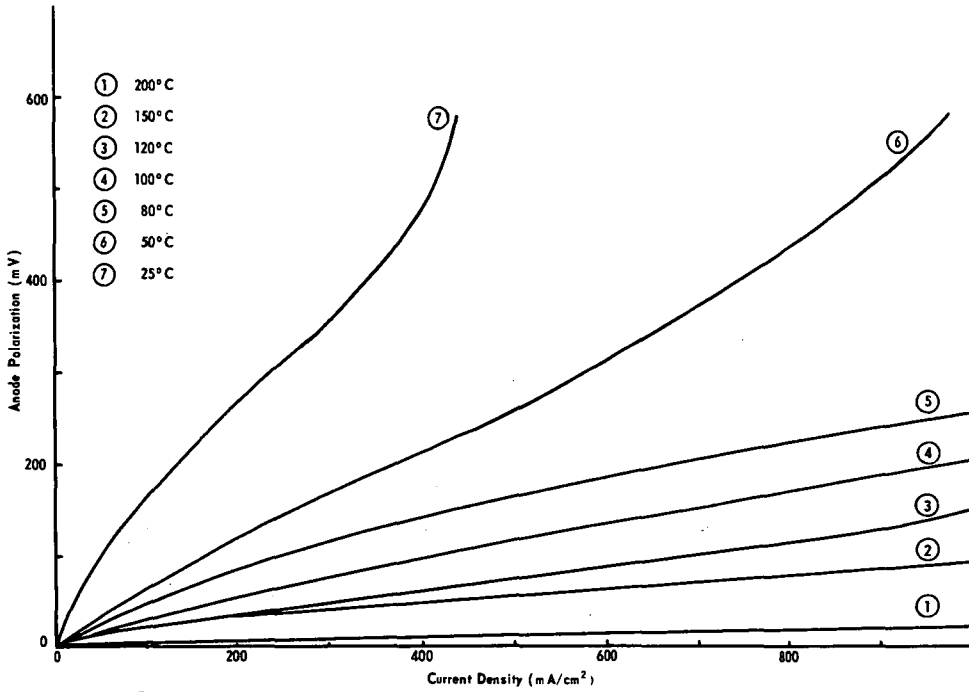
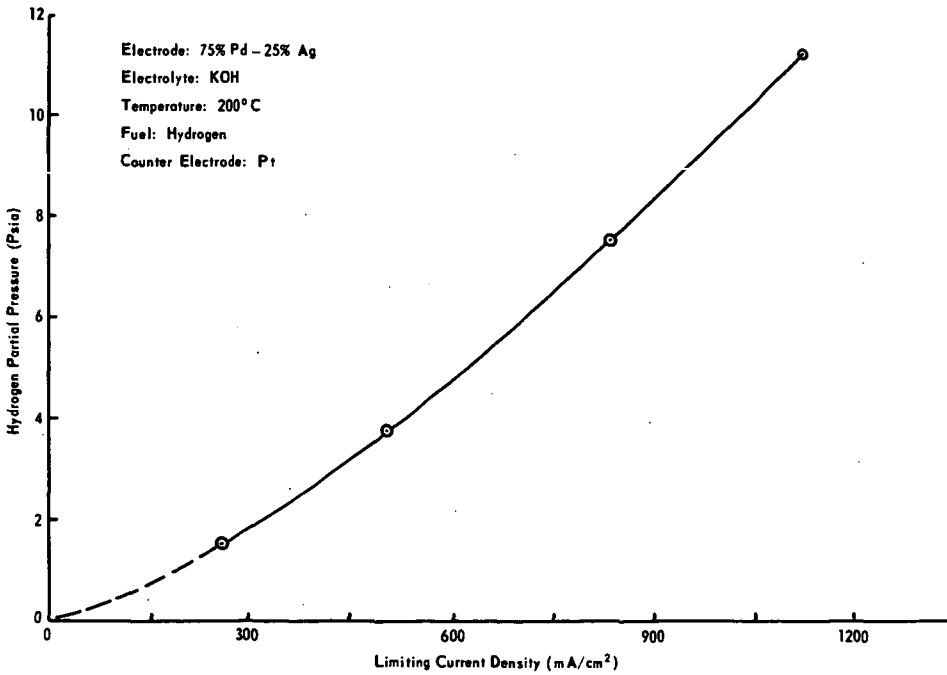Figure 3 — Polarization of Pd – Ag/H$_2$ Anode as a Function of Temperature

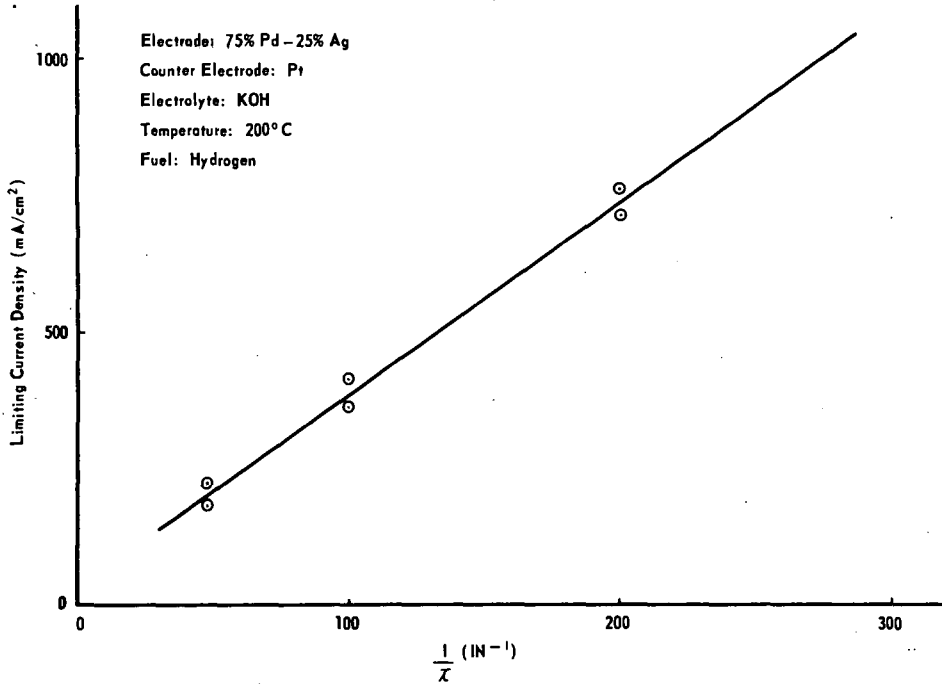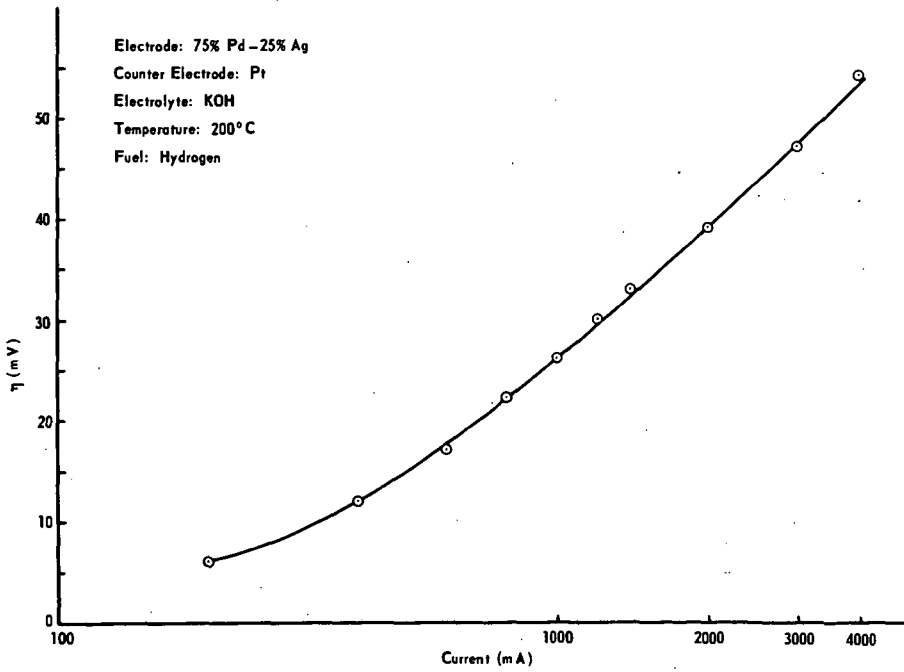Figure 4 — Limiting Current Density of Pd – Ag/H$_2$ Anode as a Function of Hydrogen Partial Pressure.

Electrode: 75% Pd – 25% Ag
Counter Electrode: Pt
Electrolyte: KOH
Temperature: 200° C
Fuel: Hydrogen

Limiting Current Density (mA/cm^2)

$\frac{1}{\chi}$ (IN^{-1})

Figure 5 – Limiting Current Density as a Function of Anode Thickness.

Electrode: 75% Pd – 25% Ag
Counter Electrode: Pt
Electrolyte: KOH
Temperature: 200° C
Fuel: Hydrogen

η (mV)

Current (mA)

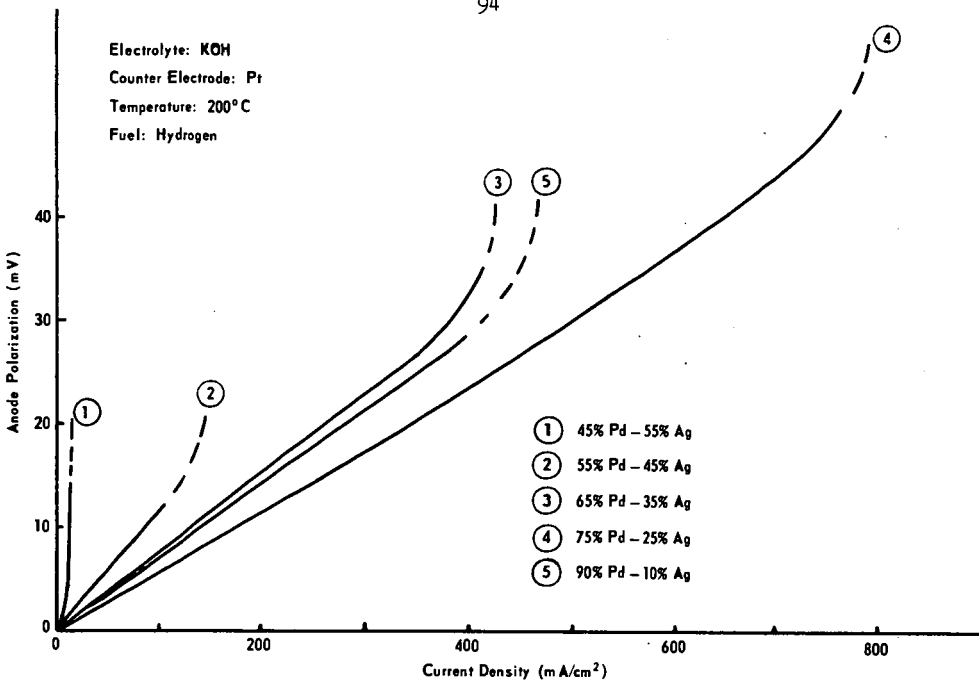Figure 6 – Tafel Plot of Pd – Ag/H$_2$ Anode
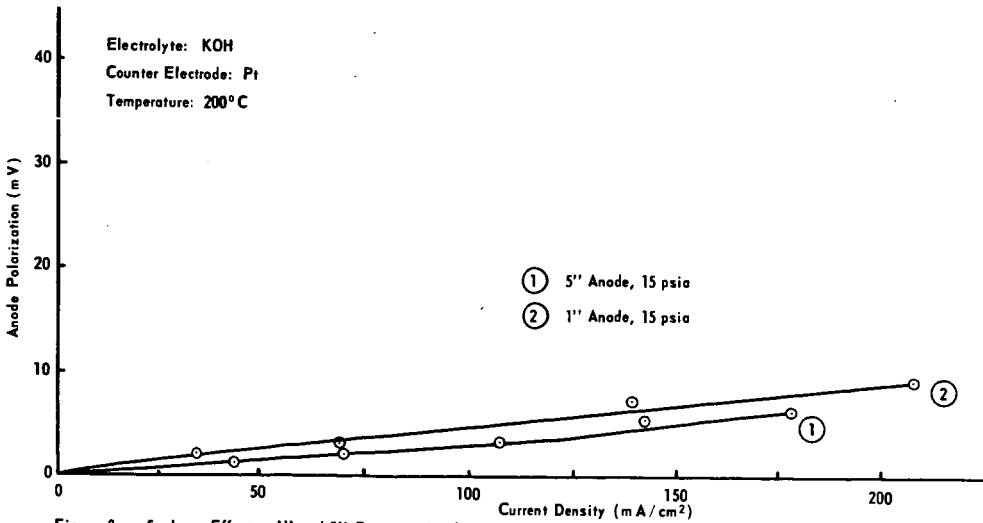
Figure 7 — Anode Polarization as a Function of Membrane Composition.

Figure 8 — Scale-up Effects: 1" and 5" Diameter Anodes